

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 724 607 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

04.08.1999 Bulletin 1999/31

(51) Int Cl.⁶: **C08G 63/78**

(86) International application number:
PCT/US94/11862

(21) Application number: 94931907.3

(22) Date of filing: 18.10.1994

(87) International publication number:
WO 95/11268 (27.04.1995 Gazette 1995/18)

(54) CONTINUOUS POLYESTER PROCESS

KONTINUIERLICHES POLYESTERVERFAHREN

PROCEDE DE PRODUCTION CONTINUE DE POLYESTER

(84) Designated Contracting States:
BE DE ES FR GB IT NL

(30) Priority: 18.10.1993 US 138312

(43) Date of publication of application:
07.08.1996 Bulletin 1996/32

(73) Proprietor: E.I. DU PONT DE NEMOURS AND
COMPANY
Wilmington Delaware 19898 (US)

(72) Inventor: BHATIA, Kamlesh, Kumar.
Newark, DE 19713-3509 (US)

(74) Representative: Jones, Alan John
CARPMAELS & RANSFORD
43 Bloomsbury Square
London, WC1A 2RA (GB)

(56) References cited:
EP-A- 0 182 351 FR-A- 2 008 068
FR-A- 2 389 649 US-A- 2 973 341
US-A- 3 480 587 US-A- 5 064 935

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 724 607 B1

Description**FIELD OF THE INVENTION**

5 [0001] An improved process for the continuous production of polyester at atmospheric pressure is disclosed.

[0002] Polyester production from terephthalic acid (TPA) or its esters, such as dimethyl terephthalate (DMT), and glycols is known. This has been accomplished by stage-wise melt polymerization of the dihydroxy ester of the bifunctional carboxylic acid, or low molecular weight oligomers thereof, under successively higher vacuum conditions. In order for the polymerization to continue to the degree needed for most commercial applications, the condensation by-products, especially ethylene glycol, must be removed from the reaction system at vacuums as high as 1-3mm Hg. Such processes require costly high vacuum equipment, multistage steam jets to create the vacuum, and N₂ purged seals and flanges to minimize leakage of air into the system. Condensate from the steam jets and organic by-products from the system end up as a waste water stream that requires treatment and contributes to volatile organic emissions to the air. The present invention provides a less costly polymerization process that can be carried out at atmospheric pressure and in a closed loop configuration that eliminates volatile organic emissions and the waste water discharge.

10 [0003] U.S. 2,973,341 (Hippe) discloses a continuous process for the production of polyester condensate and an improved continuous process for making polyethylene terephthalate from dimethyl terephthalate and ethylene glycol. The process employs liquid dimethyl terephthalate and mixes with it ethylene glycol, in an excess molar ratio of 1.5:1, to form a liquid reaction mixture in a first stage below the transesterification temperature and then carrying the liquid reaction mixture through three separate temperature controlled stages. Transesterification occurs in the second stage at a temperature of not more than 197°C; vaporous reaction products are removed in the third stage at 197°C to 230°C by passing an inert gas through the liquid reaction mixture; polycondensation occurs in the fourth stage at 230°C to 270°C for a period of time sufficient to produce a filament forming polyethylene terephthalate condensate while again passing an inert gas through the liquid reaction mixture. Ethylene glycol by-product can be recovered from the fourth stage and recycled to the second stage of the reaction.

15 [0004] U.S. 3,545,520 (Sicliari et al.) discloses an apparatus for stripping substances and lightweight fractions from polymers including a means for introducing an inert gas counter current to the polymeric material with the consequent increase in viscosity of the polymers. The apparatus permits recycling a portion of the material removed from the vessel so that the material can be recycled into the reaction container.

20 [0005] U.S. 3,469,618 (Sicliari et al.) discloses a method for stripping off volatile fractions from polyamides and polyesters involving feeding material in the form of droplets or liquid threads through an inert gaseous atmosphere, while recirculating that atmosphere.

25 [0006] U.S. 3,110,547 (Emmert) discloses a process for preparing a linear condensation polyester. In one embodiment of the invention, the polymer is extruded downwardly through a chamber while passing a current of inert gas, such as nitrogen, through the reaction vessel at a rate sufficient to keep the glycol partial pressure below 2mm Hg while maintaining a temperature between 300°C and 400°C in order to rapidly finish the polymer by converting the polymer having a degree of polymerization of from about 15 to 35 to a finished polymer with a degree of polymerization of about 70.

30 [0007] U.S. 3,390,135 (Seiner) discloses a continuous process for preparing polyester wherein the product is contacted with an inert gas which has been passed over the product in a countercurrent manner, at a regulated flow, to remove the water of esterification.

SUMMARY OF THE INVENTION

45 [0008] The invention relates to a continuous atmospheric pressure method of polymerizing a dihydroxy ester of a bifunctional carboxylic acid, or of a low molecular weight polymerizable oligomer thereof, to a product with a higher degree of polymerization (DP), in the presence of a polyester polymerization catalyst, wherein by-products of the polymerization are removed from the system by means of an inert gas.

50 [0009] This invention provides a process for preparing a linear condensation polyester, having a degree of polymerization of at least 50, by the continuous polymerization of a dihydroxy ester of a bifunctional carboxylic acid, or low molecular weight oligomer thereof, with the evolution of volatile reaction by-products including a glycol, to form a product with a higher degree of polymerization, the process being conducted at atmospheric pressure or above, comprising contacting a melt of the dihydroxy ester of a bifunctional carboxylic acid, or low molecular weight oligomer thereof, in the presence of a polyester polymerization catalyst, with an inert gas flowing counter currently in the process at a velocity of 0.2 to 5 ft/sec (0.06 to 1.5 m/sec), so that volatile reaction by-products are removed continuously by the inert gas and whereby the polymerization product is removed continuously, while the reactants are kept at a temperature sufficient to maintain the melt and to continue polymerization.

55 [0010] This process provides an improved method for producing linear aromatic polyesters, especially polyethylene

terephthalate (PET), also referred to as polyethylene glycol terephthalate. The bifunctional acid in the production of PET is terephthalic acid (TPA). The process involves the continuous production of polyethylene terephthalate, having a degree of polymerization of at least 50, from terephthalic acid and ethylene glycol by esterification, or from dimethyl terephthalate and ethylene glycol by transesterification, followed by polycondensation and polymer finishing stages. The process is conducted at atmospheric pressure or above, thereby avoiding high vacuum equipment and eliminating possible air contamination that causes product decomposition and gel formation. The process comprises the following steps:

- (a) esterifying terephthalic acid or transesterifying dimethyl terephthalate with ethylene glycol to produce dihydroxy ethyl terephthalate or its low molecular oligomers, and
- (b) intimately contacting dihydroxy ethyl terephthalate, or its low molecular weight oligomers, in melt form, with an inert gas at a velocity of 0.2 to 5 ft/sec, so that volatile reaction by-products are removed continuously by the inert gas and wherein the polymerization product is removed continuously, while the reactants are kept at a suitable temperature to maintain the melt and to continue polymerization. The above processes are conducted in the presence of a polyester polymerization catalyst.

[0011] In a preferred embodiment of the invention, a single stream of inert gas is recycled through a polymer finishing stage, a polycondensation stage and a stage wherein ethylene glycol is recovered for reuse in the process.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 is a diagrammatic flow sheet for the continuous process of the invention.

[0013] Figure 2 represents one apparatus which is suitable for carrying out the continuous polymerization of the invention, wherein material having a lower degree of polymerization is converted to material having a higher degree of polymerization.

DETAILED DESCRIPTION OF THE INVENTION

[0014] Polyethylene terephthalate is manufactured in this process by first reacting terephthalic acid (TPA) or dimethyl terephthalate (DMT) with ethylene glycol. If DMT is the starting material, a suitable transesterification catalyst such as zinc or manganese acetate is used for the reaction. Esterified DMT/TPA is polymerized as a melt at atmospheric pressure or above by intimately contacting the melt with a stream of inert gas (for example, but not limited to, N₂ or CO₂) to remove the condensation by-products, mainly, ethylene glycol. Preferably, the inert gas is preheated to about polymerization temperature or above, prior to its introduction into the polymerization equipment. It is preferred that the inert gas velocity through the polymerization equipment be in the range of 0.2 to 5 ft./sec. (0.06 to 1.5 m/sec), most preferably 0.5 to 2 ft/sec (0.15 to 0.61 m/sec), flowing counter currently to the flow of the melt. The vapor leaving the polymerization equipment (after a finishing stage and a polycondensation stage) is fractionated to recover ethylene glycol for recycle. The nitrogen stream is then cleaned up and recycled. Thus, the overall process operates as a closed loop system which avoids environmental pollution and integrates ethylene glycol purification and its recycle into the process.

[0015] Catalysts for facilitating the polymerization are any one or more polyester polymerization catalysts known in the prior art to catalyze such polymerization processes, such as, but not limited to, compounds of antimony, germanium and titanium. Antimony trioxide (Sb₂O₃) is an especially effective catalyst which may be introduced, for convenience, as a glycolate solution in ethylene glycol. Examples of such catalysts are found in U.S. 2,578,660, U.S. 2,647,885 and U.S. 2,789,772, which are incorporated herein by reference.

[0016] Dihydroxy esters of bifunctional carboxylic acids used in the processes described herein are monomeric compounds that can polymerize to a polymer. Examples of such compounds are bis(2-hydroxyethyl) terephthalate, bis(4-hydroxybutyl) terephthalate, bis(2-hydroxyethyl) naphthalenedioate, bis(2-hydroxyethyl) isophthalate, bis[2-(2-hydroxyethoxy)ethyl] terephthalate, bis[2-(2-hydroxyethoxy)ethyl] isophthalate, bis[(4-hydroxymethylcyclohexyl)methyl] terephthalate, bis[(4-hydroxymethylcyclohexyl)methyl] isophthalate, and a combination of bis(4-hydroxybutyl) terephthalate and their oligomers. Mixtures of these monomers and oligomers may also be used.

[0017] By a "polymerizable oligomer" is meant any oligomeric material which can polymerize to a polyester. This oligomer may contain low molecular weight polyester, and varying amounts of monomer. For example, the reaction of dimethyl terephthalate or terephthalic acid with ethylene glycol, when carried out to remove methyl ester or carboxylic groups usually yields a mixture of bis(2-hydroxyethyl) terephthalate, low molecular weight polymers (oligomers) of bis(2-hydroxyethyl) terephthalate and oligomers of mono(2-hydroxyethyl) terephthalate (which contains carbonyl groups). This type of material is referred to herein as "polymerizable oligomer".

[0018] Polyesters produced by the process include, but are not limited to, poly(ethylene terephthalate), poly(1,4-buty-

lene terephthalate), poly(ethylene naphthalenedioate), poly(ethylene isophthalate), poly(3-oxa-1,5-pentadiyl terephthalate), poly(3-oxa-1,5-pentadiyl isophthalate), poly[1,4-bis(oxyethyl)cyclohexyl terephthalate] and poly[1,4-bis(oxyethyl)cyclohexyl isophthalate]. Poly(ethylene terephthalate) is an especially important commercial product.

[0019] The process avoids high vacuum polymerization processes characteristic of the conventional art. Advantages of the process are a simpler flow pattern, lower operating costs and the avoidance of steam jets, hot wells and atmosphere emissions. The process also has environmental advantages due to the elimination of volatile organic emissions and waste water discharge. Furthermore, polymerization is conducted in an inert environment. Therefore, there is less decomposition and gel formation which results in better product quality. Ethylene glycol and inert gas (e.g., N_2 or CO_2) are recycled continuously. The process is described in greater detail with reference to Figures 1 and 2.

[0020] Figure 1 is a diagrammatic flow sheet for the continuous process of the invention. Reactant materials TPA (or its dimethyl ester, DMT) and ethylene glycol are supplied continuously to an esterification column (2) for esterification (or transesterification) to DHET and its low DP oligomers. The resulting esterified or transesterified product is an oligomer with a low degree of polymerization (DP). The resulting DP is from 1-2 if the starting material is DMT. If TPA is the starting material, the resulting oligomer usually has a higher DP, in the range of from about 3-7. The molten reaction product formed in the esterification column (2) is conducted through transfer line (4) to a prepolymerization column (6) for polycondensation. A suitable polyester polymerization catalyst, such as Sb_2O_3 , may be added at this point. The prepolymer, exiting the esterification column with a degree of polymerization from 15-30, is conducted through transfer line (8) to finisher (10) in order to finish the polymer by raising the degree of polymerization to about 50 to about 150, preferably about 60 to about 100. The finisher (10) is maintained at a temperature greater than about $260^\circ C$ but not high enough to result in polymer decomposition. A temperature range of about $270^\circ C$ to $300^\circ C$ is preferred. The polymerization product is continuously removed from the finisher through line (30). An inert gas, preferably nitrogen, is heated in heater (12) at a temperature of from about $280^\circ C$ to $320^\circ C$ and is introduced through line (14) into the finisher to flow counter current to the direction of polymer flow in order to remove volatile reaction by-products, primarily ethylene glycol. The inert gas flows through the finisher (10) and then through line (16) to prepolymerization column (6) removing volatile reaction by-products, which are mainly ethylene glycol, in that reaction column. The hot inert gas stream containing organic vapors, which are mainly ethylene glycol with minor amounts of methanol, water, and some thermal decomposition products, exits the prepolymerization column through line (18) and enters the glycol recovery column (20) where glycol is recovered from the stream and refined without the need for additional external heat. The recovered glycol is recycled to the esterification column (2) through line (22). The inert gas stream containing the volatile organics, such as acetaldehyde, exits the glycol recovery column through line (24) and enters an adsorption bed (26), such as an activated carbon bed, wherein the organic volatiles are adsorbed producing a clean nitrogen stream which can be heated and returned to the finisher (10). Thus, the nitrogen is employed in a closed loop and all processing equipment is operated at atmospheric pressure (or above, as is necessary to ensure the flow of nitrogen through the equipment in the loop). The inert gas flowing in the polymerization equipment (6) and (10) has a velocity of between about 0.2 to 5 ft/sec (0.06 to 1.5 m/sec), preferably 0.5 to 2 ft/sec (0.15 to 0.61 m/sec). The quantity of inert gas introduced into the system is sufficient so that the partial pressure of the by-products is maintained below the equilibrium pressure of the by-products with the melt in order to provide for the continuous polymerization. The quantity of inert gas is between about 0.2-0.5 pounds (0.09 to 0.23 kg) for each pound (0.45 kg) of polyethylene terephthalate produced. The adsorption bed (26) can be purged to remove the adsorbed products. The adsorbed products are transferred by line (28) to a combustion device, such as a boiler, (not shown) where they are converted to carbon dioxide and water by combustion thus completing an environmentally clean, emissions free process.

[0021] Figure 2 illustrates one apparatus which is suitable for carrying out the continuous polymerization of the invention particularly for use with the high viscosity material and degree of polymerization encountered in the finisher (10) of Figure 1. It consists of a horizontal, agitated cylindrical vessel (32). The esterified DMT or TPA, or a low molecular weight oligomer thereof, is continuously introduced as stream (34) at one end of the vessel (32) and a preheated inert gas, such as nitrogen, is continuously introduced as stream (38) at the other end, so as to provide a counter current flow to the polymer flow. The nitrogen stream (38) carrying reaction by-product vapors, mostly ethylene glycol, leaves as stream (40). The polymerized product, polyethylene terephthalate, is removed as stream (36). The flow rates of streams (34) and (36) are coordinated to be equivalent to each other and controlled so as to provide the desired inventory of the melt in the finisher, usually about equivalent to 1 to 2 hours times the flow rate, with melt level at about 1/3 to 1/2 the height of the vessel. The quantity of nitrogen introduced into the system is sufficient so that the partial pressure of the evolving reaction by-products is maintained at less than the equilibrium pressure of the by-products with the, for example, poly(ethylene) terephthalate (PET) melt, so as to provide adequate driving force to remove ethylene glycol from the melt into the gas stream. The diameter of the vessel is designed so that the superficial velocity of the inert gas stream is about 0.5 to 2 ft/sec (0.15 to 0.61 m/sec).

[0022] The vessel is equipped with an agitator (42) which can be rotated at a controlled speed. The mechanical design of the agitator is such that

- (a) the walls of the vessel are wiped;
- (b) a large interfacial area of at least 10 ft²/ft³ (32.8 m²/m³), preferably greater than 30 ft²/ft³ (98.43 m²/m³), is created;
- (c) the surface area is renewed frequently; and
- (d) good mixing is provided.

[0023] One design which achieves the above specified criteria, is a rotating disc contactor consisting of several discs mounted on a shaft (in a fashion similar to that in conventional continuous polymerizers) but the discs in this design are sieve plates, with large open area, which allow well distributed cross flow of the inert gas vapors.

EXAMPLES 1 - 9

[0024] Examples 1 - 9 were conducted in a test tube heated to 280 to 295°C by placing it in a temperature controlled sand bath. The test tube was equipped with means to introduce preheated N₂ at a controlled rate near the bottom and an outlet was created near the top of the test tube to allow N₂ to exit. Except for Example 9, 5 g samples of monomer, prepared at a DuPont commercial plant site by transesterifying DMT with EG, were placed in the test tube along with 180 to 1600 ppm of antimony, added as a Sb₂O₃ catalyst. The catalyst level was not found to affect the polymerization rate significantly and higher levels led to greyish discoloration of the product. Therefore, except for Examples 3, 5, and 6 which had catalyst levels of 1600, 400 and 900 ppm, respectively, all other Examples were at lower catalyst levels as shown in Table 1. In Example 9, a 10 g sample was employed and a Mn catalyst used for transesterification was rendered inactive by reacting with phosphoric acid, before adding the antimony catalyst. This also did not effect the kinetics measurably.

[0025] In Examples 8 and 9, the temperature was ramped from 230°C to 285°C over a 10 to 15 minute period. This allowed the initial polymerization to occur at lower temperatures and minimized volatilization of the low DP oligomers into the N₂ stream.

[0026] When the monomer melted in the tube, N₂ was introduced at a flow rate such that the superficial gas velocity was in the range expected for a commercial scale operation. The nitrogen velocities employed are shown in Table 1. For the examples where a range of velocities is shown, such as 0.2-0.6 ft/sec (0.06 to 0.18 m/sec) in Example 9, it means that the velocity was at the lower value at the start of the reaction and gradually increased to the higher value as the polymerization proceeded. N₂ was introduced below the melt causing the melt to lift up and allowing it to fall along the tube walls to create interfacial area (estimated at > 30 ft²/ft³ (98.43 m²/m³)), and provide surface renewal and good mixing. Experiments were conducted for 12 to 105 minutes and the resulting PET product was analyzed for molecular weight distribution by GPC. The number average degree of polymerization calculated from GPC data for each sample are shown in Table 1. The values were independently confirmed by measurements of intrinsic viscosity.

TABLE 1

EXAMPLE	POLYMERIZATION Time (Min.)	CATALYST ppm Sb	N ₂ VELOCITY ft./sec. (m/sec)	NO AVG. DP
1	12	225	0.3 - 0.6 (0.09-0.18)	24
2	21	180	0.3 - 1.0 (0.09-0.30)	44
3	21	1600	0.3 (0.09)	39
4	39	225	0.3 - 1.3 (0.09-0.40)	54
5	39	400	0.6 (0.18)	54
6	42	900	0.6 (0.18)	57
7	60	225	0.3 - 1.0 (0.09-0.30)	64
8	105	200	0.2 - 1.9 (0.06-0.58)	182
9	90	280	0.2 - 0.6 (0.06-0.18)	70

EXAMPLE 10

[0027] Polymerization of the same monomer used in Example 9 was studied on a microbalance apparatus in a stream of nitrogen in order to determine the impact of nitrogen velocity on mass transfer. A small sample, 63.6 mg, was suspended in a heated glass tube having a 25 mm inside diameter through which nitrogen flowed at a rate of 330 cc/min. Temperature of the sample was monitored by a thermocouple mounted close to the sample, while controlling the heat input to the glass tube. The progress of polymerization was monitored by observing the weight loss due to the evolution of reaction by-product, ethylene glycol.

[0028] The sample was heated to 288°C and then held at that temperature for 90 minutes while maintaining the nitrogen flow rate. The velocity of nitrogen in the glass tube was calculated as 0.077 ft/sec (0.023 m/sec). Due to the small size of the sample, there was a very large surface to volume ratio, estimated at over 180 ft²/ft³ (591 m²/m³). In spite of such a large area (several times that of Examples 1-9) the rate of polymerization was slow due to the low nitrogen velocity. At the end of 90 minutes the polymer obtained and analyzed by GPC had a number average DP of only about 14. The need for adequate nitrogen velocity was confirmed by this experiment.

EXAMPLE 11

[0029] The same monomer used in Example 9 was polymerized in a laboratory apparatus of the type shown in Figure 2 which was constructed to operate under the conditions disclosed in Example 12 for a commercial scale operation.

[0030] The apparatus consisted of a 6 inch (15.2 cm) glass tube with an inside diameter of 1 inch (2.5 cm) which was placed in a tube furnace equipped with temperature control. The tube was fitted with an agitator of 1/8 inch (3.2 mm) diameter coiled aluminum wire which provided mixing, surface renewal and wiping of the inside tube wall. The agitator was rotated by Use of a motor having a variable speed gear reducer. It is estimated that the device provided a surface area of about 60 ft²/ft³ (197 m²/m³) of the melt. The polymer melt temperature was monitored by means of a thermocouple inserted into the tube at each of its two ends.

[0031] The tube was filled with 37.6 g of monomer and placed in the furnace. The furnace temperature was raised to a sufficient temperature to melt the monomer. When the monomer was molten, the agitator was started and preheated nitrogen was flowed at a velocity of about 0.5 ft/sec (0.15 m/sec) through the tube. The temperature set point was then raised to 290°C to effect polymerization. When the melt temperature inside the tube reached 290°C, the velocity of the nitrogen was raised to 1.1 ft/sec (0.34 m/sec). Polymerization was continued for 90 minutes while controlling these operations under the above stated conditions. The actual temperature near the nitrogen outlet end varied from around 270 to 299°C. The agitator speed was initiated at 15 RPM, but was reduced to 8 RPM after about 20 minutes and then further reduced to around 3-4 RPM after another 20 minutes as the melt became more viscous.

[0032] At the end of 90 minutes of polymerization, two samples of the resulting PET were analyzed by GPC. The number average DP was calculated to be 79 and 89, respectively. This is higher than the typical value required for yarn and staple use.

[0033] To check the feasibility of higher nitrogen velocities, the velocity was raised to 1.45 ft/sec (0.44 m/sec) during the last 3 minutes of operation. No polymer carryover was observed. Just before shutting down, the velocity was increased to over 3 ft/sec (0.91 m/sec) and was found to be feasible.

EXAMPLE 12

[0034] Example 12 illustrates the process of the invention for operating continuously at a commercial scale of approximately 100 million pounds (4.536 x 10⁷ kg) per year. Referring to Figure 1, about 12,150 lbs/hr (5511 kg/hr) of prepolymer of approximately 20 DP are fed to finisher (10), maintained at between 285-295°C, and contacted counter currently with a stream of nitrogen heated to about 300°C and flowed at a rate of 1000 standard cubic feet per minute (SCFM) (28.3 m³/min). The flow rate is equivalent to 0.39 pound (0.20 kg) of nitrogen per pound (0.45 kg) of PET produced. The finisher is 7 ft (2.13 m) in diameter and 21 ft (6.4 m) long. Polyethylene terephthalate, polymerized to a number average DP of 81, is withdrawn at a rate of 12,000 lbs/hr (5443 kg/hr) through line (30) while the level in the finisher is controlled such that about 1/3 of the finisher volume remains filled with polymer melt. The melt inventory is thus equivalent to about 100 minutes or 1-2/3 hours of PET throughput rate. The finisher (10) is equipped with an agitator to provide an interfacial area of about 50 square feet per cubic foot (164 m²/m³) of the melt. It provides frequent surface renewal and good mixing of the melt. The superficial gas velocity of the nitrogen stream is 1.2 ft/sec (0.37 m/sec) under the actual operating conditions. The nitrogen stream leaving the finisher (10) through line (16) contains approximately 150 pounds of the ethylene glycol evolved in the finisher. The partial pressure of ethylene glycol in the stream is about 11 mm Hg (146 Pa).

[0035] The nitrogen stream leaving the finisher (10) through line (16) is then fed to the prepolymerizer (6) to provide counter current contact with the esterification product of about 1.5 average DP, produced by transesterification of DMT with ethylene glycol, entering the prepolymerizer (6) through line (4) at a rate of about 14,550 pounds/hour (6600 kg/hr).

[0036] The prepolymerizer tower is 6 ft (1.83 m) in diameter and 30 ft (9.14 m) high. The interior of the tower is designed so as to provide intimate staged contact between the melt and the nitrogen vapor such that the hold up time of the melt in that column is about 20 minutes or 1/3 hour. The total time for polymerization, including the 1-2/3 hours in the finisher is thus about 2 hours or less.

[0037] The prepolymerizer is operated at 280°C. A somewhat lower temperature may be maintained at the top of the tower to minimize volatilization of the lower molecular weight oligomers. The nitrogen velocity in the prepolymerizer is about 1 ft/sec (0.30 m/sec) near the bottom of the tower and about 1.4 ft/sec (0.47 m/sec) near the top of the tower.

[0038] The hot nitrogen vapors exit the prepolymerizer (6) through line (18) containing about 2550 pound of ethylene glycol, along with small amounts of other components, such as very low DP oligomers, methanol from the end groups left unreacted during transesterification and minute quantities of high volatile organics, such as acetaldehyde, which may be present. The nitrogen stream is fed to the bottom of the ethylene glycol recovery column (20) through line (18). The column is 4 ft (1.22 m) in diameter and the nitrogen velocity averages about 1.8 ft/sec (0.55 m/sec). Heat is removed at the top of the column to cool the nitrogen to near the ambient temperature. Essentially all the ethylene glycol is condensed and leaves the bottom of the column through line (22) as a hot liquid stream of about 150°C. It is recycled through line (22) to the esterification column (2).

[0039] The small amount of oligomers entrained with the nitrogen stream leaving the prepolymerizer (6) react with the large excess of glycol at the bottom of the EG recovery column, reverting back to the monomer and are recycled along with the glycol stream to the esterification column. The uncondensed organics, such as acetaldehyde leave the EG recovery column along with the nitrogen through line (24) and are fed to an adsorption bed (26) of activated carbon. Volatile organic vapors are absorbed on the bed thus cleaning up the nitrogen stream. The nitrogen stream is heated to about 300°C and recycled to the finisher. The adsorption bed (26) is periodically purged, when it nears saturation, to remove adsorbed organics which are sent to the boiler house and converted to carbon dioxide and water. A small amount of nitrogen may be purged from the nitrogen loop, and replenished with an equivalent amount of fresh nitrogen to keep the levels of impurities in the loop low. Such a nitrogen purge may be used for the periodic purging of the adsorption bed.

Claims

1. A process for preparing a linear condensation polyester, having a degree of polymerization of at least 50, by the continuous polymerization of a dihydroxy ester of a bifunctional carboxylic acid, or low molecular weight oligomer thereof, with the evolution of volatile reaction by-products including a glycol, to form a product with a higher degree of polymerization, the process conducted at atmospheric pressure or above, comprising contacting a melt of the dihydroxy ester of a bifunctional carboxylic acid, or low molecular weight oligomer thereof, in the presence of a polyester polymerization catalyst, with an inert gas flowing countercurrently in the process at a velocity of 0.2 to 5 ft/sec (0.06 to 1.5 m/sec), so that volatile reaction by-products are removed continuously by the inert gas and whereby the polymerization product is removed continuously, while the reactants are kept at a temperature sufficient to maintain the melt and to continue polymerization.
2. The process of Claim 1 wherein the dihydroxy ester of a bifunctional carboxylic acid is selected from the group consisting of bis(2-hydroxyethyl) terephthalate, bis(4-hydroxybutyl)terephthalate, bis(2-hydroxyethyl) naphthalenedioate, bis(2-hydroxyethyl) isophthalate, bis[2-(2-hydroxyethoxy)ethyl] terephthalate, bis[2-(2-hydroxyethoxy)ethyl] isophthalate, bis[(4-hydroxymethylcyclohexyl)methyl] terephthalate, and bis[(4-hydroxymethylcyclohexyl)methyl] isophthalate.
3. A process for the continuous production of polyethylene terephthalate, having a degree of polymerization of at least 50, from terephthalic acid and ethylene glycol by esterification followed by the process stages of polycondensation and polymer finishing, the process conducted at atmospheric pressure or above, comprising:
 - (a) esterifying terephthalic acid with ethylene glycol to produce dihydroxy ethyl terephthalate or its low molecular oligomers,
 - (b) intimately contacting a melt of dihydroxy ethyl terephthalate, or its low molecular weight oligomers, with an inert gas flowing in the process countercurrently at a velocity of 0.2 to 5 ft/sec (0.06 to 1.5 m/sec), so that volatile reaction by-products, including ethylene glycol, are removed continuously by the inert gas which is recycled in the system, and wherein the polymerization product is removed continuously, while the reactants are kept at a temperature sufficient to maintain the melt and to continue polymerization, said process conducted in the presence of a polyester polymerization catalyst.
4. A process for the continuous production of polyethylene terephthalate, having a degree of polymerization of at least 50, from dimethyl terephthalate and ethylene glycol by transesterification followed by the process stages of polycondensation and polymer finishing the process conducted at atmospheric pressure or above, comprising:
 - (a) transesterifying dimethyl terephthalate with ethylene glycol to produce dihydroxy ethyl terephthalate or its low molecular oligomers,
 - (b) intimately contacting a melt of dihydroxy ethyl terephthalate, or its low molecular weight oligomers, with

an inert gas flowing in the process countercurrently at a velocity of 0.2 to 5 ft/sec (0.06 to 1.5 m/sec), so that volatile reaction by-products, including ethylene glycol, are removed continuously by the inert gas which is recycled in the system, and wherein the polymerization product is removed continuously, while the reactants are kept at a temperature sufficient to maintain the melt and to continue polymerization, the process conducted in the presence of a polyester polymerization catalyst.

- 5 5. The process of Claim 1, 3, or 4 wherein the catalyst is selected from compounds of antimony, germanium and titanium.
- 10 6. The process of Claim 1, 3, or 4 wherein the inert gas is preheated to about polymerization temperature or above polymerization temperature prior to contacting it with the melt.
7. The process of Claim 1, 3, or 4 wherein the quantity of the inert gas introduced into the system is sufficient so that the partial pressure of the by-products is maintained at less than the equilibrium pressure of the by-products with the melt.
- 15 8. The process of Claim 1, 3, or 4 wherein the volatile reaction by-products are recovered and the inert gas is continuously recycled for reuse in the process.
- 20 9. The process of Claim 1, 3, or 4 wherein a single stream of inert gas is recycled through the polymer finishing stage, a polycondensation stage and a stage wherein ethylene glycol is recovered for reuse in the process.
10. The process of Claim 1, 3, or 4 wherein the inert gas is selected from N_2 and CO_2 .
- 25 11. The process of Claim 3 or 4 wherein the temperature of the finishing stage is $270^\circ C$ to $300^\circ C$.
12. The process of Claim 1, 3, or 4 wherein the interfacial area is at least $30 \text{ ft}^2/\text{ft}^3$ ($98.43 \text{ m}^2/\text{m}^3$).
13. The process of Claim 1, 3, or 4 wherein the velocity of the inert gas flow is 0.2 to 2 ft/sec (0.06 to 0.61 m/sec).
- 30 14. The process of Claim 3 or 4 wherein the quantity of inert gas is between about 0.2-0.5 pounds (0.09 to 0.23 kg) for each pound (0.45 kg) of polyethylene terephthalate produced.

35 Patentansprüche

1. Verfahren zum Herstellen eines linearen Kondensationspolyesters mit einem Polymerisationsgrad von mindestens 50 durch die kontinuierliche Polymerisation eines Dihydroxyesters einer bifunktionellen Carbonsäure oder niedermolekulargewichtigen Oligomeren davon mit der Entwicklung von flüchtigen Reaktionsnebenprodukten, einschließlich eines Glykols, unter Bilden eines Produktes mit einem höheren Polymerisationsgrad, wobei das Verfahren bei Atmosphärendruck oder darüber durchgeführt wird, aufweisend in Kontakt bringen einer Schmelze des Dihydroxyesters einer bifunktionellen Carbonsäure oder niedermolekulargewichtigen Oligomeren davon in der Anwesenheit eines Polyesterpolymerisationskatalysators mit einem Inertgas, welches gegenströmend in dem Verfahren mit einer Geschwindigkeit von 0,2 bis 5 Fuß/Sek (0,06 bis 1,5 m/Sek) fließt, so daß flüchtige Reaktionsnebenprodukte kontinuierlich durch das Inertgas entfernt werden, und wodurch das Polymerisationsprodukt kontinuierlich entfernt wird, während die Reaktanten bei einer Temperatur gehalten werden, die ausreichend ist, die Schmelze aufrechtzuerhalten, und Polymerisation fortzusetzen.
2. Verfahren nach Anspruch 1, wobei der Dihydroxyester einer bifunktionellen Carbonsäure aus der Gruppe bestehend aus Bis(2-hydroxyethyl)terephthalat, Bis(4-hydroxybutyl)terephthalat, Bis(2-hydroxyethyl)naphthalindioat, Bis(2-hydroxyethyl)isophthalat, Bis[2-(2-hydroxyethoxy)ethyl]terephthalat, Bis[2-(2-hydroxyethoxy)ethyl]isophthalat, Bis[(4-hydroxy-methylcyclohexyl)methyl]terephthalat und Bis[(4-hydroxymethylcyclohexyl)-methyl]isophthalat ausgewählt wird.
3. Verfahren für die kontinuierliche Herstellung von Polyethylterephthalat mit einem Polymerisationsgrad von mindestens 50 aus Terephthalsäure und Ethylenglykol durch Veresterung, gefolgt von den Verfahrensstufen der Polykondensation und Polymerfertigstellung, wobei das Verfahren bei Atmosphärendruck oder darüber durchgeführt wird, aufweisend:

(a) Verestern von Terephthalsäure mit Ethylenglykol unter Herstellen von Dihydroxyethylterephthalat oder dessen niedrigmolekularer Oligomere,

(b) inniges in Kontakt bringen einer Schmelze von Dihydroxyethylterephthalat oder dessen niedrigmolekulargewichtiger Oligomere mit einem Inertgas, welches in dem Verfahren gegenströmend mit einer Geschwindigkeit von 0,2 bis 5 Fuß/Sek (0,06 bis 1,5 m/Sek) fließt, so daß flüchtige Reaktionsnebenprodukte, einschließlich Ethylenglykol, kontinuierlich durch das Inertgas entfernt werden, welches in dem System im Kreislauf geführt wird, und wobei das Polymerisationsprodukt kontinuierlich entfernt wird, während die Reaktanten bei einer Temperatur gehalten werden, die ausreichend ist, die Schmelze aufrechtzuerhalten und Polymerisation fortzuführen, wobei das Verfahren in der Anwesenheit eines Polyesterpolymerisationskatalysators durchgeführt wird.

4. Verfahren für die kontinuierliche Herstellung von Polyethylenterephthalat mit einem Polymerisationsgrad von mindestens 50 aus Dimethylterephthalat und Ethylenglykol durch Umesterung, gefolgt von den Verfahrensstufen der Polykondensation und Polymerfertigstellung, wobei das Verfahren bei Atmosphärendruck oder darüber durchgeführt wird, aufweisend:

(a) Umestern von Dimethylterephthalat mit Ethylenglykol unter Herstellen von Dihydroxyethylterephthalat oder dessen niedrigmolekularer Oligomere.

(b) inniges in Kontakt bringen einer Schmelze von Dihydroxyethylterephthalat oder dessen niedrigmolekulargewichtiger Oligomere mit einem Inertgas, welches in dem Verfahren gegenströmend mit einer Geschwindigkeit von 0,2 bis 5 Fuß/Sek (0,06 bis 1,5 m/Sek) fließt, so daß flüchtige Reaktionsnebenprodukte, einschließlich Ethylenglykol, kontinuierlich durch das Inertgas entfernt werden, welches in dem System im Kreislauf geführt wird, und wobei das Polymerisationsprodukt kontinuierlich entfernt wird, während die Reaktanten bei einer Temperatur gehalten werden, die ausreichend ist, die Schmelze beizubehalten und Polymerisation fortzuführen, wobei das Verfahren in der Anwesenheit eines Polyesterpolymerisationskatalysators durchgeführt wird.

5. Verfahren nach Anspruch 1, 3 oder 4, wobei der Katalysator aus Verbindungen von Antimon, Germanium und Titan ausgewählt wird.

6. Verfahren nach Anspruch 1, 3 oder 4, wobei das Inertgas auf etwa Polymerisationstemperatur oder oberhalb Polymerisationstemperatur vor dem Kontaktbringen von ihm mit der Schmelze vorerhitzt wird.

7. Verfahren nach Anspruch 1, 3 oder 4, wobei die Menge des in das System eingeführten Inertgases ausreichend ist, so daß der Partialdruck der Nebenprodukte bei weniger als dem Gleichgewichtsdruck der Nebenprodukte mit der Schmelze aufrechterhalten wird.

8. Verfahren nach Anspruch 1, 3 oder 4, wobei die flüchtigen Reaktionsnebenprodukte gewonnen werden, und das Inertgas kontinuierlich im Kreislauf für Wiederverwendung in dem Verfahren geführt wird.

9. Verfahren nach Anspruch 1, 3 oder 4, wobei ein einzelner Strom von Inertgas durch die Polymerfertigstellungsstufe, eine Polykondensationsstufe und eine Stufe, wo Ethylenglykol für Wiederverwendung in dem Verfahren gewonnen wird, geführt wird.

10. Verfahren nach Anspruch 1, 3 oder 4, wobei das Inertgas aus N_2 und CO_2 ausgewählt wird.

11. Verfahren nach Anspruch 3 oder 4, wobei die Temperatur der Fertigstellungsstufe $270^\circ C$ bis $300^\circ C$ beträgt.

12. Verfahren nach Anspruch 1, 3 oder 4, wobei der Grenzflächenbereich mindestens $30 \text{ Fuß}^2/\text{Fuß}^3$ ($98,43 \text{ m}^2/\text{m}^3$) beträgt.

13. Verfahren nach Anspruch 1, 3 oder 4, wobei die Geschwindigkeit des Inertgasflusses 0,2 bis 2 Fuß/Sek (0,06 bis 0,61 m/Sek) beträgt.

14. Verfahren nach Anspruch 3 oder 4, wobei die Menge von Inertgas zwischen etwa 0,2-0,5 Pfund (0,09 bis 0,23 kg) für jedes Pfund (0,45 kg) hergestelltes Polyethylenterephthalat liegt.

Revendications

1. Procédé de préparation d'un polyester de condensation linéaire, ayant un degré de polymérisation d'au moins 50, par la polymérisation continue d'un ester dihydroxylé d'un acide carboxylique bifonctionnel, ou d'un oligomère de bas poids moléculaire de celui-ci, avec le dégagement de sous-produits réactionnels volatils comprenant un glycol, pour former un produit ayant un degré plus élevé de polymérisation, le procédé étant effectué à ou au-dessus de la pression atmosphérique, comprenant la mise en contact d'un bain fondu de l'ester dihydroxylé d'un acide carboxylique bifonctionnel, ou d'un oligomère de bas poids moléculaire de celui-ci, en présence d'un catalyseur de polymérisation de polyesters, avec un gaz inerte s'écoulant à contre-courant dans le procédé à une vitesse de 0,06 à 1,5 m/s (0,2 à 5 ft/s), de façon que les sous-produits réactionnels volatils soient enlevés en continu par le gaz inerte et par lequel le produit de polymérisation est extrait en continu, tandis que les réactifs sont maintenus à une température suffisante pour entretenir le bain fondu et pour poursuivre la polymérisation.
2. Procédé selon la revendication 1 dans lequel l'ester dihydroxylé d'un acide carboxylique bifonctionnel est choisi dans le groupe constitué du téréphtalate de bis(2-hydroxyéthyle), du téréphtalate de bis(4-hydroxybutyle), du naphthalenedioate de bis(2-hydroxyéthyle), de l'isophtalate de bis(2-hydroxyéthyle), du téréphtalate de bis[2-(2-hydroxyéthoxy)éthyle], de l'isophtalate de bis[2-(2-hydroxyéthoxy)éthyle], du téréphtalate de bis[4-hydroxy-méthylcyclohexyl)méthyle], et de l'isophtalate de bis[4-hydroxy-méthylcyclohexyl)méthyle].
3. Procédé pour la production continue de poly(téréphtalate d'éthylène), ayant un degré de polymérisation d'au moins 50, à partir d'acide téréphtalique et d'éthylèneglycol par estérification suivie des étapes de traitement de polycondensation et de finissage du polymère, le procédé étant effectué à ou au-dessus de la pression atmosphérique, comprenant:
 - a) l'estérification d'acide téréphtalique avec de l'éthylèneglycol pour produire du téréphtalate d'éthyle dihydroxylé ou ses oligomères de bas poids moléculaire,
 - b) la mise en contact intime d'un bain fondu de téréphtalate d'éthyle dihydroxylé ou de ses oligomères de bas poids moléculaire, avec un gaz inerte s'écoulant dans le procédé à contre-courant à une vitesse de 0,06 à 1,5 m/s (0,2 à 5 ft/s), de façon que les sous-produits réactionnels volatils, parmi lesquels l'éthylèneglycol, soient enlevés en continu par le gaz inerte qui est recyclé dans le système, et dans lequel le produit de polymérisation est extrait en continu, tandis que les réactifs sont maintenus à une température suffisante pour entretenir le bain fondu et pour poursuivre la polymérisation, ledit procédé étant effectué en présence d'un catalyseur de polymérisation de polyesters.
4. Procédé pour la production continue de poly(téréphtalate d'éthylène), ayant un degré de polymérisation d'au moins 50, à partir de téréphtalate de diméthyle et d'éthylèneglycol par transestérification suivie des étapes de traitement de polycondensation et de finissage du polymère, le procédé étant effectué à ou au-dessus de la pression atmosphérique, comprenant:
 - a) la transestérification de téréphtalate de diméthyle avec de l'éthylèneglycol pour produire du téréphtalate d'éthyle dihydroxylé ou ses oligomères de bas poids moléculaire,
 - b) la mise en contact intime d'un bain fondu de téréphtalate d'éthyle dihydroxylé ou de ses oligomères de bas poids moléculaire, avec un gaz inerte s'écoulant dans le procédé à contre-courant à une vitesse de 0,06 à 1,5 m/s (0,2 à 5 ft/s), de façon que les sous-produits réactionnels volatils, parmi lesquels l'éthylèneglycol, soient enlevés en continu par le gaz inerte qui est recyclé dans le système, et dans lequel le produit de polymérisation est extrait en continu, tandis que les réactifs sont maintenus à une température suffisante pour entretenir le bain fondu et pour poursuivre la polymérisation, le procédé étant effectué en présence d'un catalyseur de polymérisation de polyesters.
5. Procédé selon la revendication 1, 3, ou 4 dans lequel le catalyseur est choisi parmi les composés d'antimoine, de germanium et de titane.
6. Procédé selon la revendication 1, 3, ou 4 dans lequel le gaz inerte est préchauffé à peu près à la température de polymérisation ou au-dessus de la température de polymérisation avant d'être mis en contact avec le bain fondu.
7. Procédé selon la revendication 1, 3, ou 4 dans lequel la quantité du gaz inerte introduit dans le système est suffisante pour que la pression partielle des sous-produits soit maintenue inférieure à la pression d'équilibre des sous-produits avec le bain fondu.

8. Procédé selon la revendication 1, 3, ou 4 dans lequel les sous-produits réactionnels volatils sont récupérés et le gaz inerte est recyclé en continu pour être réutilisé dans le procédé.
- 5 9. Procédé selon la revendication 1, 3, ou 4 dans lequel un seul flux de gaz inerte est recyclé dans l'étape de finition du polymère, une étape de polycondensation et une étape dans laquelle l'éthylèneglycol est récupéré pour être réutilisé dans le procédé.
10. Procédé selon la revendication 1, 3, ou 4 dans lequel le gaz inerte est choisi parmi N_2 et CO_2 .
- 10 11. Procédé selon la revendication 3 ou 4 dans lequel la température de l'étape de finissage est de 270°C à 300°C.
12. Procédé selon la revendication 1, 3, ou 4 dans lequel la surface interfaciale est au moins de 98,43 m²/m³ (30 ft²/ft³).
- 15 13. Procédé selon la revendication 1, 3, ou 4 dans lequel la vitesse de l'écoulement de gaz inerte est de 0,06 à 0,61 m/s (0,2 à 2 ft/s).
14. Procédé selon la revendication 3 ou 4 dans lequel la quantité de gaz inerte est comprise entre environ 0,09 et 0,23 kg (environ 0,2-0,5 livres) pour chaque 0,45 kg (chaque livre) de poly(téréphtalate d'éthylène) produit.
- 20
- 25
- 30
- 35
- 40
- 45
- 50
- 55

FIG. 1

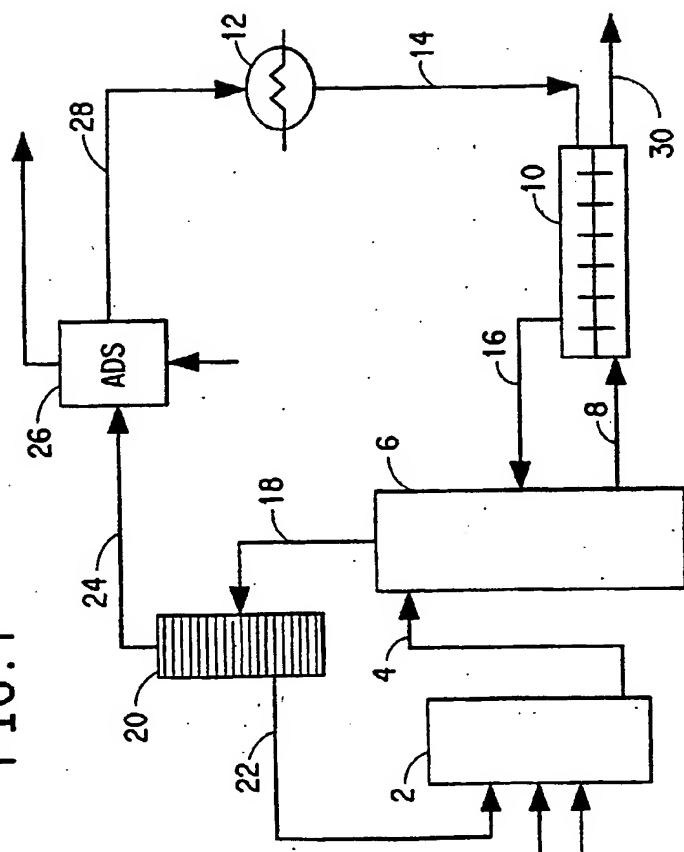


FIG. 2

